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Review of Western European and Japanese Iron and Steel Industry Exemplary Water Pollution Control Technology

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Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

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Review of Western European and Japanese Iron and Steel Industry Exemplary Water Pollution Control Technology

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16. ABSTRACT The report gives results of a literature survey of current Western European and Japanese water pollution control technology in the iron and steel industry. Further information was obtained through personel communication. Recycle technology was identified as being practiced to a high degree by the Japanese. A variable recycle rate was found to be practiced at British and Western European steel plants. Summaries of typical pollution control operations are described and comparative date are provided.

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ABSTRACT

Current Western European and Japanese water pollution control technology in the iron and steel industry was identified by means of a literature survey and telephone and TELEX communications. We found that the Japanese favor recycle technology whereas British and Western European steel plants practice a variable recycle rate. Summaries of typical pollution control operations are described and comparative data are provided.

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SECTION 1

INTRODUCTION

In 1971, the International Iron and Steel Institute set up a Committee on Environmental Matters to demonstrate its active support of measures to conserve and improve the quality of world environmental conditions. It did not attempt to minimize the complexity of the overall problems faced by the steel industry. The institute did believe, however, that acceptable solutions could be achieved by an exchange of information among industries on a world-wide basis, as well as by voluntary cooperation with local control and conservation organizations.

At present, significant problems remain to be solved. In response to this, the iron and steel industries of the United States, Japan and West Germany have been steadily increasing investments in pollution control. In the United States, the steel industry ranks among the leading manufacturers in capital expenditures for pollution control. A survey conducted by McGraw-Hill[1], shows that between 1971 and 1972, the United States steel industry spent $400 million on air and water pollution control - about 8 percent of the total spent ty all manufacturing industries. In 1973, the steel industry's pollution control expenditure was $276 million or 13.6 percent of the total expenditures of the steel industry. By 1976, that figure increased to an extimated $517 million spent on pollution control or an estimated 18.8 percent of total expenditures.

The figures available for Germany and Japan also indicate a steady growth in pollution control investment. Between 1970 and 1974, the German investment grew from 7.3 to 12 percent of the total capital investment. Similarly, the Japanese industry increased its investment from 4 to 20 percent in a matter of 10 years.

The U.S. iron and steel industry thus compares very favorably with foreign plants. Most of the Japanese and Western European plants, however, are relatively new, which makes it easier to implement the use of newer equipment and techniques.

The objective of this study was to survey foreign techniques in water pollution control and to identify any advances which might be studied for transfer to the Unived States iron and steel industry. Since the limited fresh water supply in Japan and areas of Western Europe necessitate a high degree of water recycle, this survey focused on water pollution control techniques of iron and steel plants practicing either a high degree of water

[1]Iron and Steel International, June, 1974, pp. 228-237

recycle or exemplary pollution abatement capability.

In the report, the Japanese iron and steel plants are considered as one group, and the Western European plants as another one. The guidelines set by the different countries have been obtained, and the actual performance of the exemplary plants are compared with these guidelines wherever possible. This report also includes conclusions and recommendations which are concerned with the applicability of some of these exemplary techniques. Some recommendations have been made suggesting improvements in methodology for collecting information on a project of this nature.

SECTION 2

CONCLUSIONS

In general, Japanese and British steel plants use more saline water than their U.S. counterparts, who usually rely on fresh water sources. From the available data, Bethlehem Steel's Sparrows Point is the only American plant using seawater. Since fresh water is cheap and readily available in the U.S., American plants recycle from 15 to 80 percent of the fresh water. Japanese plants, however, recycle about 90 percent of the fresh water used.

The British steel plants also have a high degree of fresh water recycling, 2 to 90 percent of the water used from all sources. Higher degrees of recycle are practiced in the inland plants, whereas the smaller figures are for coastal plants using sea water. Plants using saline water recycle only their fresh water. The techniques used by the British and other Western European plants are similar to those of American plants. For example, the British Carbonization Research Association has been conducting research on the biological oxidation process for effluent control.

The Japanese industry uses some relatively modern techniques, examples of which are:

(1) dry coke quenching,
(2) ion exchange resin method for pickling rinse waste water treatment.

Based on discussions with our in-house experts, we conclude that:

(1) U.S. iron and steel plants do not practice water recycling to as high a degree as the foreign plants, primarily due to the availability of cheap and plentiful fresh water in the U.S.
(2) Japanese plants use modern techniques because their plants are newer. U.S. plants could also implement these techniques, given sufficient incentive and space.

Table 1 is provided for comparison of U.S. and foreign plants. (More information is clearly needed from Western European plants.) As can be seen, the dry coke quenching (DCQ) and the ion exchange processes are exemplary techniques used by the Japanese industry. As can be seen by comparing data on pollution control investments, the U.S. iron and steel plants rate favorably with foreign plants.

It is not feasible in this survey to perform an economic analysis of the applicability of transferring foreign techniques. In order to generate specific data it would be necessary to do an in-depth study on a case by case basis. This type of analysis was beyond the scope of this survey report.

TABLE 1

COMPARISON OF TECHNIQUES

METHOD	U.S.A.	JAPAN	BRITAIN	W.GERMANY	ITALY
1. Use of seawater	Used at Bethlehem Steel's Sparrows Point Plant	✓ *	✓	N.A. **	N.A.
2. Degree of freshwater recycle	A very wide range, depending on the age of the plant and location	around 90%	around 90%	N.A.	N.A.
3. Physical treatment (settling, filtration, etc.)	✓	✓	✓	✓	✓
4. Ultrahigh Rate filtration	✓	✓	N.A.	N.A.	N.A.
5. Dry Coke Quenching process	Not in use	✓	Not in use	N.A.	N.A.
6. Ion Exchange Process for the Pickle Liquor Wastes	Not in use	✓	In the beginning stages	N.A.	N.A.
7. Biological Oxidation Process	✓	✓	✓	✓	✓
8. Pollution Control Investment (% of Capital Investment)	≃18.8%	16-20%	N.A.	≃12% ***	N.A.

*✓ Technique currently in use
**N.A. Information not available
*** Estimate

SECTION 3

RECOMMENDATIONS

Further research into foreign iron and steel pollution control should be conducted. In order to evaluate the feasibility of technology transfer and to verify the specific operational state-of-the-art in Europe and Japan, more in-depth, operational information on a wide range of steel plants is required. There is also more information available than this survey covered. For example, new guidelines are currently being formulated by government and industrial committees. This information, combined with specifics obtained through site visits, should result in a more accurate prediction of the utility of technology transfer of foreign water recycle and pollution control techniques.

A general study of steel plant parameters correlated with effluent levels would answer some applicability questions. Ranges of plant size, age, output, and water source characteristics could be matched to ranges of pollution capability, yielding data helpful in technology transfer analysis. It must be noted that recycle and pollution control systems are designed on a case by case basis. Thus, before a new pollution control system can be recommended, a case by case analysis of the above variables should be performed.

We would also suggest that distance and language barriers could be eliminated by on-site activity. Delays in translating questions and receiving information would thus be minimized. On-site interviews might also alleviate some of the hesitation of steel companies to discuss their pollution control data. An intergovernmental agreement or project might also facilitate access to these plants.

Another area of research would be in-depth studies of individual exemplary plants. Exemplary plants with the newest, model equipment can be either those recently constructed, such as Nippon Kokan Corporation's Ogishima plant or older plants with recent pollution control retrofit.

SECTION 4

THE JAPANESE STEEL INDUSTRY

The Japanese iron and steel industry is one of the more sophisticated in the world. The Japanese have built many modern steelmaking facilities during the last decade. With every year, regulations for environmental control in Japan have become progressively stricter. The Japanese industry currently spends 16 to 20 percent of its capital investment on pollution control[2]. As can be seen from Figure 1, the proportion of pollution control investment has increased from 4 to 20 percent in a span of 10 years[3]. This 20 percent compares with a 18.8 percent for the United States and about 12 percent for West Germany.

According to Mr. Minora Mizuno (General Manager, Environmental Control Department, Nippon Kokan Corporation), the following are recent developments in water pollution control in Japan[4]:

(a) Over 90 percent of the water used at the Japanese Steel Works is recovered.

(b) Coke Oven Gas Cooling H_2O is treated by the activated Sludge Process. Aerobic bacteria remove the ammonia and phenol.

OPERATING DATA FOR A JAPANESE IRON AND STEEL PLANT

We shall examine more closely the operation statistics of an exemplary Japanese iron and steel plant[5], which has invested about 20 percent of its capital in pollution control equipment. The plant has one blast furnace with a capacity of $4{\cdot}3 \times 10^6$ Kg of pig iron per day and two basic oxygen furnaces that each process $0{\cdot}25 \times 10^6$ Kg. of steel each. Seawater is used as a coolant for the plant's electric power station. When the water leaves the system, there is no further contamination except thermal. This water must be returned to the sea with a maximum temperature of $38^{\circ}C$. This is a difficult standard to meet during the summer. No information has been provided on corrosion levels or corrosion inhibiting techniques used by the industry. This seawater should be treated before use as a coolant. Some of the commonly used techniques are:

[2]Chemical and Engineering News, July 28, 1975, pp. 10-11.
[3]Transactions of the Iron and Steel Institute of Japan, Figure 12, Vol. 17, No. 8, 1977, pp. 441.
[4]Steel Times, May, 1973, pp. 388.
[5]Unpublished information provided by Dr. K.S. Goto, Tokyo Institute of Tech.

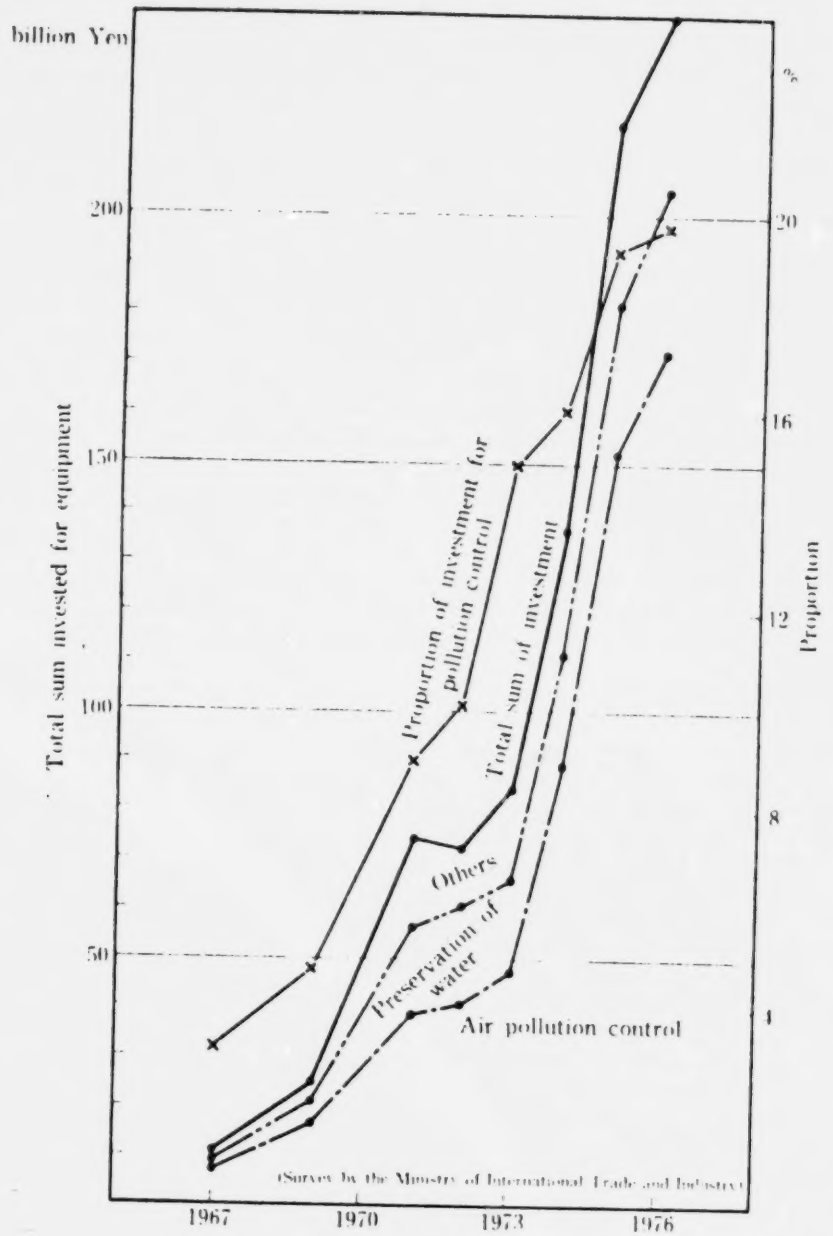

Figure 1.Investment in Japans steel industry for pollution control equipment.
Trans Iron & Steel Institute of Japan,Vol 17,No 8,1977,p441
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1. Ion Exchange
2. Electrodialysis
3. Reverse Osmosis

The daily intake of process water is $1{\cdot}3 \times 10^9$ Kg. of which $1{\cdot}27 \times 10^9$ Kg. or 97.8 percent is recycled. 30×10^6 Kg. (2.2 percent) is consumed on a daily basis in this plant.

The plant has four water storage pools and nine units of wastewater treatment systems, of which two use the activated sludge process with activated carbon.

Table 2 compares the operating characteristics of this plant with Japanese regulation values. As can be seen, operating values are uniformly better than the regulation value. The regulation values give us an idea of the Japanese effluent guidelines.

The data in Table 2 were obtained with considerable effort as Japanese steel plants are very secretive about their operating values. It is our feeling that further efforts should be made to obtain the operating data of all exemplary plants, as well as the transfer of technology from this plant to the United States.

Some of the pollution control efforts of Nippon Kokan Corporation (NKK) and Nippon Steel Corporation (NSC) were exemplary. NKK's efforts are briefly described as well as several specific techniques used by NKK and NSC.

THE NIPPON KOKAN CORPORATION (NKK)

NKK, the second largest steel corporation in Japan, spent about $163 million for pollution control between 1971 and 1974[6]. It is now calculated that steelmaking pollution costs are about $6.00 per 1000 Kg. ingot. NKK's Ogishima project, scheduled for completion by the end of 1978, has been heralded as the most modern plant in the world[7]. Its operating values are similar to those shown in Table 2. The Keihin works is currently being phased out and is being replaced by the Ogishima plant. The first phase is already operational.

The Fuluyama and Keihin Works

The water treatment equipment at Fukuyama incorporates design technology obtained from the United States:

- The cascade method of recirculation, which separates the water according to its quality.
- Ultra-high-rate filtration for treating direct contact water at hot and cold strip mills.

The plants at Fukuyama and Keihin have very high water recirculation

[6]Iron and Steel International, June 1974, pp. 205-227.
[7]Iron and Steel International, Vol. 50, No. 2, April, 1977, pp. 75.

TABLE 2

COMPOSITIONS OF WATER AFTER TREATMENT

(Average Values of Operation Data Over a Period of 4 Months)

CONSTITUENT	BOF DUST CATCHER WATER		SPRAYWATER OF CONTINUOUS CASTING SLABS		COKE OVEN WATER (ACTIVATED SLUDGE)		ROLLING MILL WATER	
	A	B	A	B	A	B	A	B
pH	8.0- 8.3	5.8- 8.6	8.2- 8.3	5.8- 8.6	6.6- 7.1	5.8- 8.6	7.6- 7.7	5.8- 8.6
COD (mg/1)	4	<20	4 - 5	<20	9 -31	30	4	<20
TSS	14 -15	<30	<5	<30	5 -12	30	5 - 8	<30
Oils (mg/1)	<3	<3	<3	<3	<3	<3	<3	<3
Soluble Iron (mg/1)	0.70	3	<0.02	3	--	--	<0.02	--
Soluble Manganese (mg/1)	<0.02	1	<0.02	1	--	--	<0.02	--
Zinc (mg/1)	0.70	1	--	--	--	--	--	--
Cyanides (mg/1)	--	--	--	--	0,08-0.36	<1	--	--
Phenol (mg/1)	--	--	--	--	<0,05	<0,5	--	--

A = actual values; B = regulation values; -- = data not available

Private communication from Dr. Goto

rates: 88 percent at the Keihin and 93 percent at the Fukuyama Works. Part of the water for cleaning blast furnace gas is circulated through a thickener to trap suspended solids and is then reused. Another part is used for cooling the blast furnace slag. Pollutants in coke oven waste ammonia liquor such as phenol and cyanides are removed by an activated sludge process. At Fukuyama, a 2400 m^3/day treatment plant was installed at the cost of about $3 million. In order to eliminate any coloration which might be present, NKK utilizes a treatment plant, wherein coagulation, sedimentation, and filtration activities take place.

Water discharged in the cold strip mill is treated by dissolved air flotation with coagulating agents. Water from surface treating processes is discharged after reduction, neutralization, and sedimentation.

Water containing high concentrations of hydrochloric acid is first treated to recover the acid and then reused. A 60 x 10^3 Kg/day capacity drying plant is maintained at the Keihin Works, where sludge is neutralized, dehydrated, and then dried in a rotary kiln for recovering iron materials.

At the Keihin Works, a $1.0 million incineration plant processes oily sludge and waste at a rate of about 800 x 10^3 Kg/month. The oil separated from the waste is used for fuel. At the Fukuyama Works, a $1.5 million incineration plant processes oily wastes and other refuse at a capacity of 4·2 x 10^6 Kg/month.

SPECIFIC PROCESSES USED BY THE JAPANESE IRON AND STEEL INDUSTRY

The Japanese steel industry utilizes some new and exemplary techniques for controlling its water pollution, such as dry coke quenching and ion exchange treatment of pickle liquor water.

Dry Coke Quenching (DCQ)

The dry coke quenching process is a novel technique devised by Russian scientists and perfected by the Japanese (initially by the Nippon Steel Corporation). It has not yet been implemented in any American plant.

The process has the following advantages:

- it is a closed system.
- it eliminates the use of water
- it saves energy.
- it reduces pollution.
- it yields a better quality coke (no impurities and a better crystalline structure).

In DCQ, hot coke pushed out from the ovens is quenched with recirculating inert gas instead of water. Figure 2 represents the flow chart for the DCQ process. Red hot coke is carried to the top of a quenching chamber and dumped into its pre-chamber. It gradually descends from the pre-chamber to the cooling chamber, where inert gas absorbs heat from the coke. The cooled coke is then discharged from the bottom of the quenching chamber. The gas,

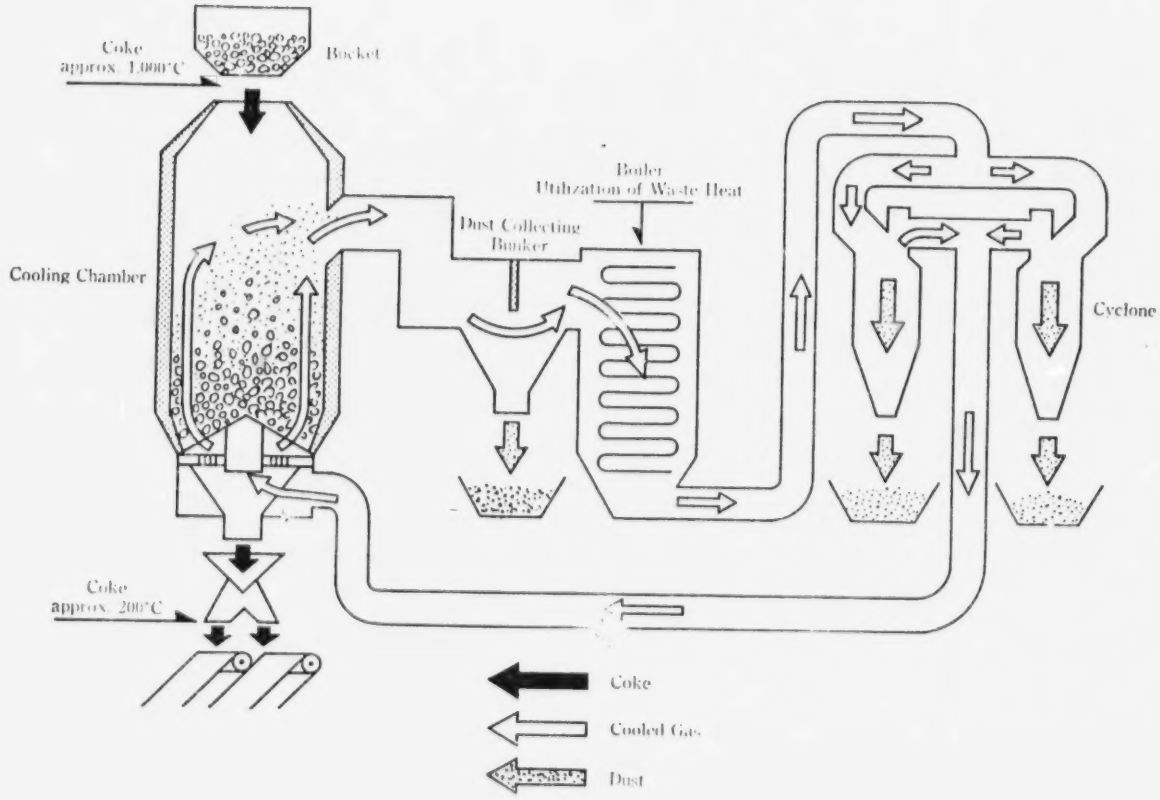

FIGURE 2. DRY COKE QUENCHING PROCESS
Transactions Iron & Steel Institute of Japan, July, 1977, Reprinted with permission.

heated to temperatures of about 800°C, is led to a waste heat boiler, after its dust has been removed, to produce the stream for heat recovery.[8] The cooled gas is sent back to the cooling chamber for circulation. NKK currently has 5 DCQ units, each with a quenching capacity of about 70 x 10^3 Kg/hr.

Ion Exchange Resin Method for Pickling Rinse Water Treatment

The pickling process is a very important step in an integrated steel plant. Some 50 percent of the products produced in an integrated steel works undergoes acid pickling.[9] Water is used both for diluting the sulfuric or hydrochloric acid in the acid bath and for washing to steel in the rinse tank. This accounts for a large quantity of water which should be treated.

The usual method for treating this wastewater is by neutralization and settling. This procedure, however, produces a large amount of sludge requiring costly disposal and treatment. NSC, in joint research with Mitsubishi Chemical Industries Limited, has developed a new process which employs direct ion exchange for the effective treatment of rinse wastewater generated by acid pickling. While already an exemplary Japanese technique, it has not yet been implemented by any American plant.

Figure 3 is the flow diagram for the NSC ion exchange process. It is much simpler than conventional processes and offers several advantages. The influent water to the ion exchange process contains 50-200 ppm Fe^{2+} ions and 100-500 ppm Cl^- ions. This rinse wastewater is directly introduced into the cation exchange resin column to remove the Fe^{2+} ions and subsequently into the anion exchange resin column to remove Cl^- ions and obtain pure water. This pure water is then recycled as rinse water.

The cation exchange resin is regenerated with highly concentrated hydrochloric acid and the regenerant waste solution is used as a supply of supplementary pickling acid. The anion exchange resin is regenerated with caustic soda and its regenerant waste solution is used as a fume scrubbed absorption solution for hydrochloric acid pickling or as an alkaline deoiling solution preceding the pickling process. Both washing and backwashing water for resin regeneration are taken from the effluent (treated water); the water is mixed with rinse wastewater for ion exchange treatment.

The process features are:

- The process is closed: no water is being discharged from the system and chemicals and agents are effectively economized.
- The process does not produce any secondary waste such as sludge.
- Because the process supplies its own pure water as it treats wastewater, water supply and drainage costs are lower than those of conventional throwaway systems.

[8]Transactions of the Iron and Steel Institute of Japan, Vol. 17, No. 8, 1977, pp. 437-438

[9]Private communication from Nippon Steel Corporation. Brochure from NSC's Plant and Machinery Division, Engineering Divisions Group on Nippon Steel's Ion Exchange Resin Method for Pickling Rinse Wastewater Treatment.

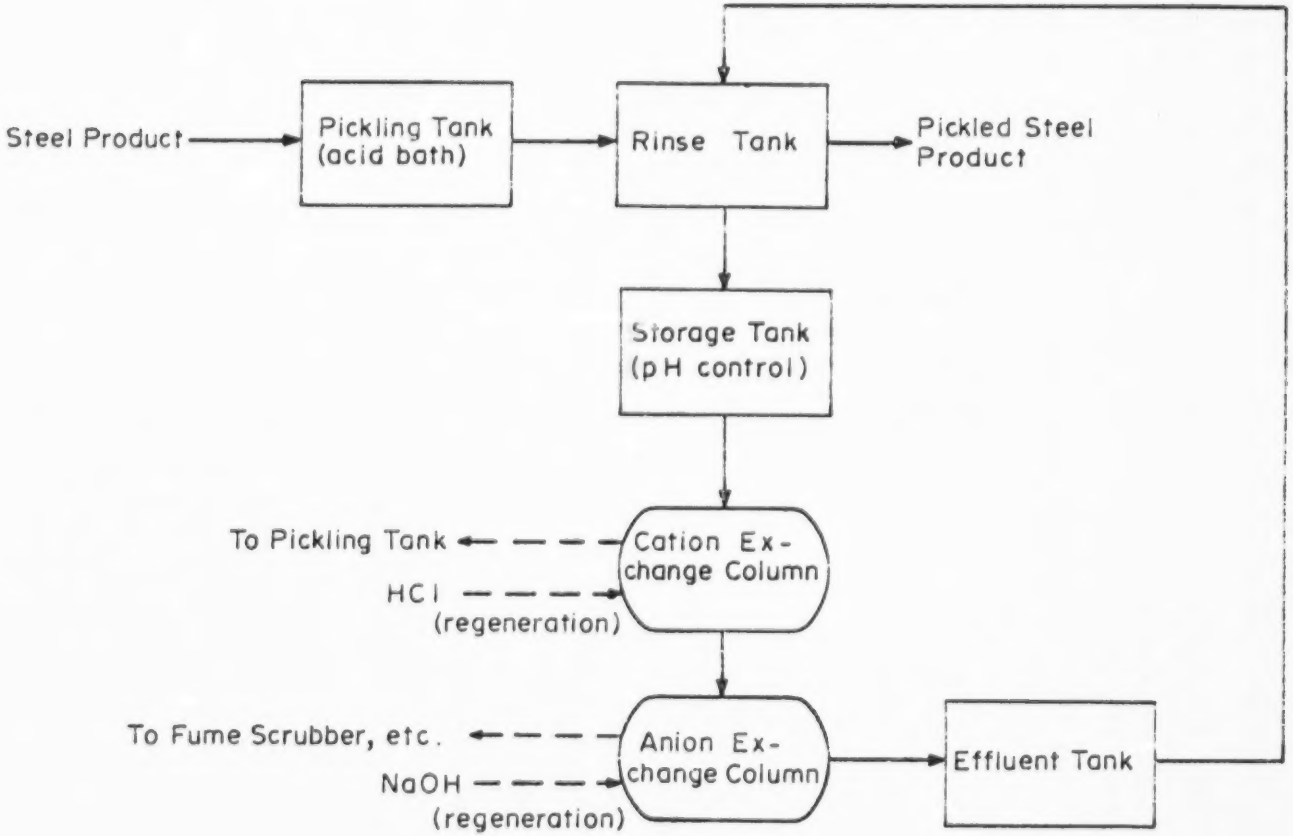

FIGURE 3. NIPPON STEEL CORPORATION ION EXCHANGE PROCESS

- The process operates automatically, reducing labor requirements.
- Because water is recycled, effective water resource utilization is assured.
- In conventional processes, rinse water is heated before rinsing begins. In this new process, water heating energy requirements are reduced.
- The process obtains pure water as its effluent and recycles it as rinse water, which in turn improves rinsing efficiency.

Nippon Steel Corporation treats rinse wastewater from the acid pickling section of its Kimitsu Works by ion exchange for purposes of environmental protection, water resource economization, and cost reduction. The commercial plant began operations in 1975.

The following are the operating data from the Kimitsu Works of Nippon Steel Corporation:

Influent flow rate	60 m^3/hr (max.)
Influent properties	Fe <200 ppm
	Cl <500 ppm
Effluent properties	Fe <0.1 ppm
	Cl <1.0 ppm
	Electric conductivity <20μmho/cm
Resin volume	Cation Exchange Resin 2.7m^3x3
	Anion Exchange Resin 5.1m^3x2
Operation practice	2 lines alternate operation
	Full automatic operation

NSC claims that despite varying influent properties, the effluent quality is extremely good and stable:

Fe <0.1 ppm
Cl <1.0 ppm
and pH ~7 (electric conductivity lower than 10μmho/cm.

The effluent is repeatedly recycled as rinse water and its clarity results in improved rinsing as compared to conventional filtered water.

The Treatment of Coke Oven Liquor[5]

The flow chart for this process in shown in Figure 4. About 80-90x10^3Kg/hr of coke oven liquor leaves the coke oven. The concentration of ammonia in this stream is about 6000-9000 mg NH_3/liter of solution. Coke oven liquor is first sent to a tar decanter, where the tar is removed. The liquor is then sent through coke filters to the ammonia-water tank. The ammonia content is reduced to about 500-1100 mg/liter. The rest of the ammonia is removed by steam stripping. This process involves stripping the NH_3 by steam under slightly alkaline conditions (pH = 8). The process stream is then neutralized by H_2SO_4. The COD of this steam is about 3000 mg/liter. The

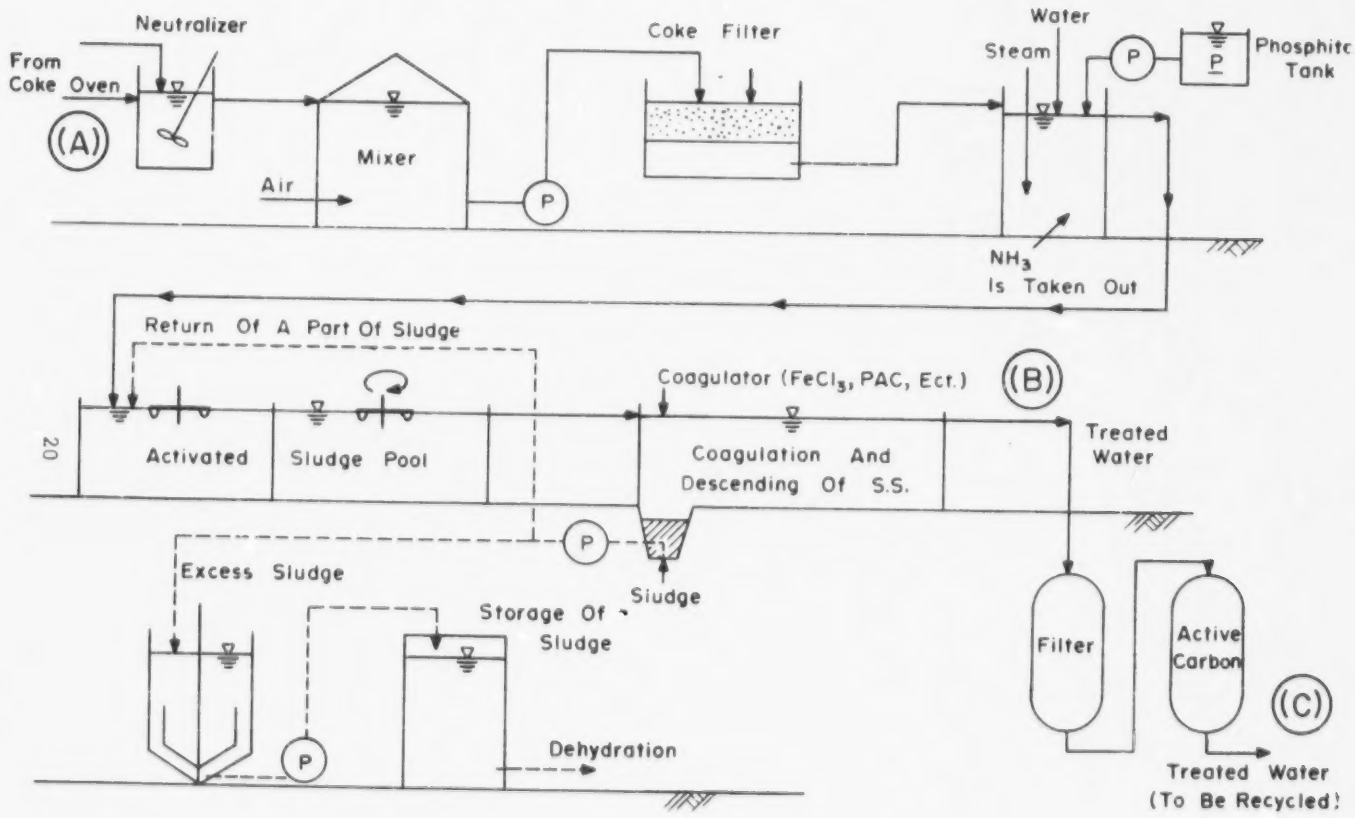

FIGURE 4. FLOW SHEET OF WATER TREATMENT FROM COKE OVEN

is sent to the activated sludge pool where the organics are decomposed by the bacteria at 20-30°C. The product stream from the activated sludge pool proceeds to the thickener where ferric chloride ($FeCl_3$) and other coagulating agents are added, reducing the COD of duct stream from this step to 90 mg/liter. From this point, the product stream flows through sand filters to remove any suspended solids and through an activated carbon tower to remove any color.

The activated sludge process involves an aerobic reaction in the presence of bacteria. The organic contaminants contained in the wasteware are biochemically oxidized by the activities of the aerobic bacteria in an aeration chamber. Bacteria thus flocculated are sedimented and separated out as sludge leaving treated water.

To ensure a proper balance in the treatment process, a sludge disposal unit is usually annexed to the system to eliminate a part of the organic phase which increased as a result of bacterial multiplication.[10] A portion of the sludge is recycled to maintain some bacterial activity.

The following operations data were obtained for a sludge disposal unit:

	Initial	Final
COD	3000 mg/1	13 mg/1
NH_3	6000-9000 mg/1	0 mg/1

The composition of the effluent stream from the process is as follows:

TSS = 5-12 mg/1
pH = 6.6 to 7.1
N-Hexane = <3 mg/1
Phenol = <0.05 mg/1

This process is usually split into two parts AB and BC, as represented in the flow chart. The second part of BC removes color. Most Japanese plants using the process implement only the first part, AB. Since all the water recovered is used for process purposes, color would not cause problems.

[10]Brochure of Japan Gasoline Company (JGC Corporation), a specialized water plant engineering company.

SECTION 5

THE WESTERN EUROPEAN STEEL INDUSTRY

The iron and steel industry in the United Kingdom, West Germany, Italy, and Spain, and Belgium was examined.

The British Steel Industry

The British Steel Corporation (BSC) is the largest iron and steel manufacturer in the United Kingdom. For a BSC plant which produces $15{\cdot}9 \times 10^9$ Kg/yr of pig iron and $24{\cdot}2 \times 10^9$ Kg/yr of crude steel, the water intake is $2{\cdot}43 \times 10^3 m^3$/day.[11]

Table 3 shows the distribution of water intake on a percentage basis.[12]

Where industries are located close to the coast, the tidal waters (non-fresh water) can be used. Fresh water, which is comparatively scarce, is recycled and reused to a great extent. The degree of recycling varies from 2.6 percent for plants using tidal water to 97.8 percent for plants at inland works. The various effluent control techniques used for different process streams are discussed in the following section.[11]

Coke Ovens and Byproducts Wastes

The disposal of these wastes, particularly the spent ammoniacal liquor, is a very difficult problem. These effluents amount to about 6500 ppm of coal carbonized and contain substantial amounts of toxic compounds such as phenols, thiocyanates, thiosulfates, chlorides, and fixed ammonia. Table 4 gives the approximate composition of spent ammoniacal liquor obtained in BSC plants.

[11]Speight, G.E., Davis, C.M., "A Review of Water Supplies and Effluent Disposal," unpublished works, private communication from Dr. R.L. Cooper of the British Carbonization Research Association (BCRA). This work is based on a survey of water usage of BSC, 1968-69.

[12]Cook, G.W., "Conservation of Water by Reuse at the Appleby-Frodingham Steel Works, Scunthorpe," Iron and Steel International, October, 1974, pp. 393-402, Table on p. 394.

TABLE 3

DISTRIBUTION OF WATER INTAKE - BSC (Appleby Frodingham) FOR THE YEAR ENDING MARCH, 1976 - (FORECASTED ESTIMATE)[12]

PROCESS	% OF TOTAL WATER INTAKE
Sinter Plants	9.3
Blast Furnace Cooling	10.2
Blast Furnace Gas Cleaning	6.4
Blast Furnace Blowing	10.8
Coke Ovens	14.7
Steelmaking - BOF	6.2
Continuous Casting	4.2
Rolling Mills	6.6
Electrical Power Generation	5.1
Steam Raising	12.0
Domestic Purposes	4.2
Slag Quenching	4.4
Miscellaneous Users	5.9
	100.0%

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[12]Iron and Steel International, October, 1974, pp. 394

TABLE 4

APPROXIMATE COMPOSITION OF SPENT AMMONIACAL LIQUOR
IN BRITISH STEEL CORPORATION PLANTS

CONSTITUENT	ppm
Total Phenols	1500
Thiocyanate	250
Thiosulphate	350
Chloride	3000
Ammonia (Free)	250
Ammonia (Fixed)	1200

The biological oxidation process (activated sludge) is quite frequently used for the disposal of these effluents. Under favorable conditions--no heavy influx, no sudden variations in temperature, a very large retention time--the process completely eliminates phenols and over 70 percent of the thiocyanate and thiosulphate present. However, the standard activated sludge treatment process does not affect the fixed ammonia content. Thus, further treatment is necessary if the standard activated sludge treatment process is used.

Blast Furnace Gas Washing Waters

The amount of solids collected in wash water (suspended solids) can be as high as 4000 ppm. These solids are usually separated as sludges after settlement and thickening.

The presence of cyanides and zinc, which are evolved from the blast furnace and are collected in the washing waters, poses additional problems. The level of these pollutants are so high that this water cannot be discharged. The water is utilized in some BSC plants, however, for evaporative reuse such as slag quenching or sinter cooling.

Fume Cleaning from Oxygen Steelmaking

The amount of fume from such oxygen steelmaking processes as the LD converted, Kaldo, rotor, and electric arc processes is substantial--$32{\cdot}5 - 43{\cdot}4 \times 10^{-3}$ Kg/Kg of steel, and the concentration of solids in the washing water is often up to about 10,000 ppm. Recirculatory systems with sedimentation and filtration units for the separation of the iron oxide sludges are normally employed.

Hot Rolling

The main contaminants here are mill scale, oils, greases, and sludges. Circulatory systems are used with scale pits, settling ponds, and oil skimming facilities for the coarser materials and clarification and filtration units for final cleansing of water before reuse. Some of the BSC plants use a

purge discharge which controls build-up of dissolved salts in the circulating water.

Acid Pickling Solutions

These pose a very difficult effluent problem. Neutralization of the sulfuric acid solutions with lime had been practiced, but this is an expensive process, and it is difficult to dispose of the sludge produced. Hence, acid recovery and regeneration processes have been given more importance. Several forms of acid recovery processes, based on the precipitation of ferrous sulfate heptahydrate or monohydrate with consequent enrichment of the acid content of the remaining liquor have been practiced.

Although sulfuric acid pickling is still being widely practiced, the trend in the British steel industry has been towards hydrochloric acid pickling combined with regeneration of the acid from the spent liquor. BSC has one of these plants currently under operation, and quite a few more are under construction.

Cold Rolling

The wastes from cold rolling are contaminated with rolling oils, detergents, and metallic particles. The effluents are initially skimmed and settled. The stream leaving this step is acidified with spent pickle liquor or an acidic rinse water to break down the emulsions. The free oil is then skimmed off and the remaining liquor neutralized and clarified.

Table 5 gives the maximum permitted effluent levels of toxic constituents from blast furnace gas cleaning water recycling systems. The data is from the Appleby-Frodingham works of the British Steel Corporation.[13]

TABLE 5

BLAST FURNACE GAS CLEANING SYSTEMS - MAXIMUM CONCENTRATION OF TOXIC CONSTITUENTS IN TREATED EFFLUENT WATER[13]

CONSTITUENT	MAXIMUM CONCENTRATION - Mg/l
Suspended solids	30.0
Dissolved solids as fluoride	25.0
Dissolved zinc or lead	1.0
Free cyanide	0.1

[13] Reprinted with permission.
[13] Cook, G.W., "Conservation of Water by Reuse at the Appleby-Frodingham Steel Works, Scunthorpe," Iron and Steel International, October 1974, pp. 401, Table on 401.

The Appleby-Frodingham Works of British Steel Corporation

The Appleby-Frodingham Works in Scunthrope is considered to be a world leader in steelmaking efficiency.[14] The extent of water reuse here has been steadily increasing. Between 1972 and 1976 the total consumption expressed as Kg of water/Kg of steel has decreased from 4.94 to 2.74. During the same period, the steel output has increased from 1.44×10^9 Kg to 4.50×10^9 Kg. The Appleby-Frodingham Works uses pnysical, chemical, and biological methods of treatment either separately or in conjunction with each other.

Physical Treatment--

The water from the primary scale settling pits is lead to four rectangular clarifiers, each equipped with a traveling bridge scraper, and then to 12 horizontal sand pressure filters. The filters, designed for high specific filtration rates of 14.8 to 16.0 $m^3/m^2/hr$, operate and clean automatically. The suspended solids content of the water is reduced to not more than 5 ppm. The filtered water is cooled to below 29^oC in a three-cell open evaporative cooling tower before being recirculated.

Chemical Treatment--

The water used for blast furnace gas cleaning is treated by a chemical process. This stream contains not only dust particles, but also contaminants such as zinc, lead, cyanide, and fluoride. Table 6 gives an analysis of the recirculating water in the blast furnace gas cleaning system. Figure 5 shows the flow diagram of this chemical process.

TABLE 6

ANALYSIS OF RECIRCULATING WATER IN BLAST FURNACE GAS CLEANING SYSTEM AT APPLEBY-FRODINGHAM[13]

CONSTITUENT	VALUE
pH	8.4
Suspended solids	30.0 mg/l
Dissolved fluoride	85.0 mg/l
Dissolved zinc	10.0 mg/l
Dissolved lead	4.0 mg/l
Free cyanide	10.0 mg/l

From Iron and Steel International, October 1974, pp. 401, Table 4

[13] Reprinted with permission

[14] "Appleby and Frodingham from the 1860's to the 1970's," Steel Times, Vol. 203, No. 6, June, 1975, pp. 407-498.

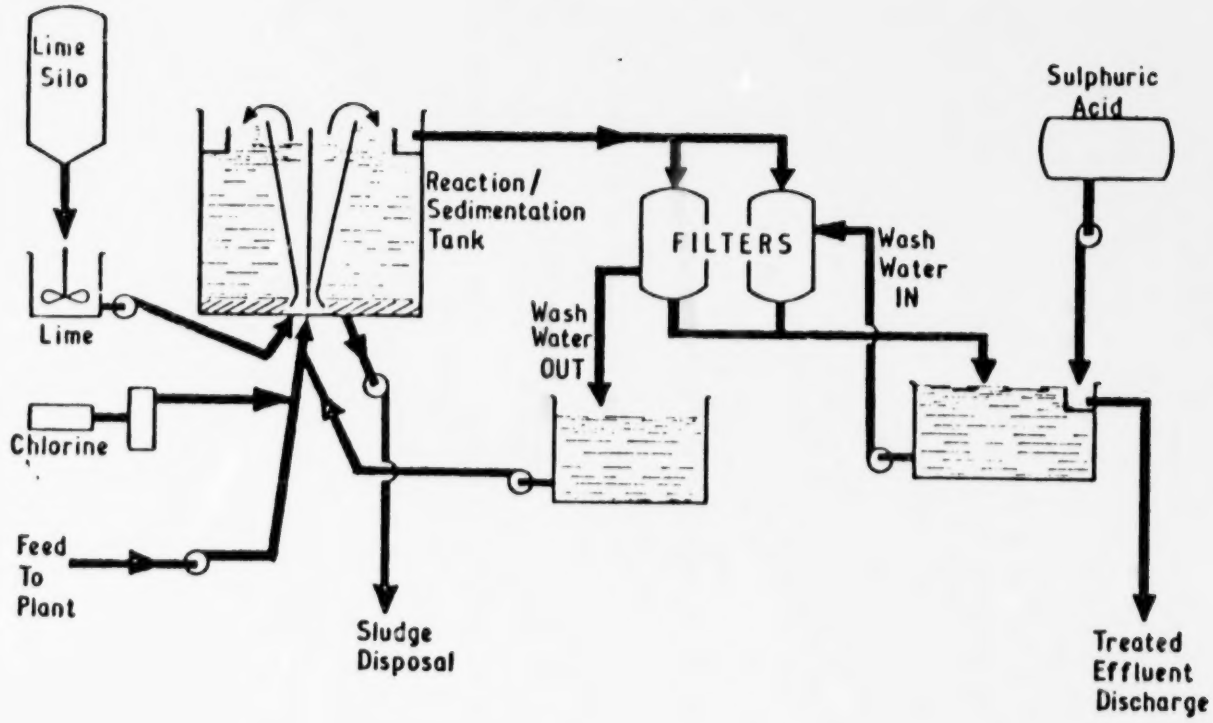

Figure 5.Effluent treatment process for removal of lead,zinc,flouride and free cyanides
Steel Times,June 1975,p496
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Lime is added to the incoming liquor to raise its pH to between 11.9 and 12.2. This alkaline condition is necessary for the oxidation of the cyanide and the precipitation of the zinc, lead, and most of the fluoride. Chlorine is injected as the liquor enters a 'circulator' reaction/sedimentation tank which is designed to give intimate mixing of the chemicals with the liquor and allow adequate time for subsequent settling of the precipitates. The precipitated solids are withdrawn as a sludge which is returned to the blast furnace gas cleaning slurry lagoon. The clarified water from the circulator is fed through pressure sand filters to a neutralization tank where sulfuric acid is added to restore the pH value to between 5 and 9. The lime silo, acid storage tank, filter wash water tank, and controls permit the plant to be self-contained and automatic in its operation. The effluents leaving this process meet the standards shown in Table 5.

Biological Treatment--

Appleby-Frodingham Works uses a central plant for the biological treatment of the effluent from three coke oven plants and two tar distillation plants. The effluents, totalling an average of 3·075 m^3/min, are collected in a reservoir with a capacity of 3180 m^3 located at the treatment plant. This liquor is diluted by adding a maximum of 0·71 m^3/min of 'clean' drainage.

The mixed liquor from the reservoir is fed into nine aeration cells, each fitted with a surface aerator. For the purpose of sludge recirculation and solids removal, the nine cells are operated as three stream flows to a separate clarifier so that under normal operation, biological sludge is returned only to those cells serving the particular clarifier.

The supernatant liquor from the clarifiers flows by gravity to a tidal storage reservoir of 3200 m^3 capacity before discharge.

The Other Western European Works

Information as detailed as that obtained from Japan and Britain was not accessible from other Western European countries. The problems were primarily caused by a language barrier, plus a hesitancy of plant officials to discuss the possibility of pollution. The information presented here is essentially from published literature available in the English language.

West Germany

German pollution control investments have been climbing sharply in the last few years. Between 1961 and 1970, 7.3 percent of total capital investment of the German steel industry was allocated to pollution control. Figures for 1973 indicate the pollution control investment to be around 12 percent. Between 1969 and 1971, the amount expended by the steel and metal working industry for investment maintenance and research represented in the aggregate 34.4 percent of all monies spent by German industry on pollution control.[15]

[15]Theegarter, H.F., Von Hartman, R.K., "Hoesch Huttenwerke's Hot Strip Mill Water Supply System," Iron and Steel Engineer, August, 1973, pp. 67-74.

The data in Table 7 represent West German effluent guidelines as of 1973.

TABLE 7

PERMISSIBLE IMPURITIES IN INDUSTRIAL WASTE WATER[15]

Temperature ^{o}C	30
Settling materials, ppm	1.0
Acidity, pH	6.5-9.5
Total Chromium ppm	4.0
Copper, ppm	3.0
Nickel, ppm	5.0
Zinc, ppm	5.0
Total iron, ppm	No limitations if no problems with treatment are to be expected.
Cyanides, ppm	1.0
Oil, ppm	0.0

[15] Reprinted with permission
Iron and Steel Engineer, August, 1973, pp.67.

It is understood that the German authorities are currently setting up even more stringent guidelines. Unfortunately, despite repeated requests, we were unable to get any specific information on the newer guidelines.

Italy

Like the Japanese and British plants, the Italsider plant at Taranto, Italy, also uses a large amount of sea water. The plant treats coke oven liquor by means of ammonia stripping and the biological oxidation process. Is also uses an interesting technique: inflatable collars are fastened across the water outlet channel to remove oil films.[16]

Spain

The Spanish pollution control guidelines date back to 1961. At the integrated plant at Sagunto considered, great attention is paid to keeping pollution to a minimum.

It is interesting to note that although some research and development is carried out, reliance on foreign 'know-how' is still strong.[17]

[16] VandenBerge, H., "Analysis, Measurement and Control at Italsider, Taranto," Iron and Steel International, Vol 49 , No. 5, October, 1976, pp.325-336.
[17] Richard, R.A.C., "The Rise of the Spanish Steel Industry," Iron and Steel International, Vol 47, No. 5, October, 1976, pp.353-360.

Belgium

Belgium's water pollution control guidelines date back to legislation of March, 1971, with revisions in August, 1974 and August, 1976. The following effluent guidelines for ferrous metal industries represent maximum additions which can be made to existing levels in the source waters. The specific guidelines of August 3, 1976, affected steel plants, cast iron foundries, hot rolling, and similar speciality works that were out of compliance:

1. Five (5) day Basic Oxygen Demand (BOD), 20°C; less than 30 mg/l.
2. Temperature limits, "slag granulating" as a separate discharge, less than 35°C.
3. For hot rolling and speciality steel works, limits for separate discharge only:
   a) petroleum ether extraction: 20 mg/l
   b) apolarity solids by carbon tetrachloride extraction, cold water: 15 mg/l

Further guidelines revisions cited in August, 1976 give the following maximums:

1.	Cyanide (oxidized by chlorination)	0.5 mg/l
2.	Chemical Oxigen Demand (COD)	500.0 mg/l
3.	Fluoride (F^-)	10.0 mg/l
4.	Sulfates (SO_4)	2000.0 mg/l
5.	Total Zinc	5.0 mg/l
6.	Total lead	1.0 mg/l
7.	Diluted iron	2.0 mg/l
8.	Diluted manganese	1.0 mg/l

These standards were proposed for a five year period, to 1981; they were published September 29, 1976, in the Belgrisch Staatsblad (the Belgian Monitor), a government publication.

APPENDIX A

SOURCES OF INFORMATION

Data for this project were obtained by:

1. Manual searches in libraries,
2. Computerized searches,
3. Telephone interview and TELEX.

The data bases that were searched through our Computer Search Center were:

APTIC: A comprehensive resource on all aspects of air pollution, its effects, prevention, and control.

BIOSIS PREVIEWS: Citations on all aspects of the biosciences and medical research.

CA CONDENSATES: Literature on chemistry, chemical engineering, and chemical aspects of the life sciences.

CHEMICAL INDUSTRY NOTES (CIN): Articles from over 75 worldwide business-oriented periodicals which cover the chemical processing industries.

COMPENDEX: Worldwide coverage of approximately 3,500 journals, publications of engineering societies, proceedings of conferences, and selected government reports and books.

ENVIROLINE: Indexing and abstracting coverage of more than 5,000 international primary and secondary source publications reporting on all aspects of the environment.

ISMEC: Abstracts of significant articles in mechanical engineering from approximately 250 journals throughout the world.

METADEX (Metals Abstracts/Alloys Index): International literature on the science and practice of metallurgy produced by the American Society for Metals (ASM) and the Metals Society (London).

NTIS: Government-sponsored research, development, and engineering plus analyses prepared by federal agencies, their contractors, or grantees.

POLLUTION ABSTRACTS: Environmentally-related literature on pollution, its sources and control.

SCISEARCH: Multidisciplinary index to the literature of science and technology, containing 90 percent of the world's significant scientific and technical literature.

SSIE (Smithsonian Science Information Exchange): Abstracts and project descriptions on ongoing research in all areas of research.

The following is a list of organizations contacted:

- Centre for Technical and Scientific Information and Documentation (TNO), Delft, Netherlands
- United Kingdom Chemical Information Service
- Danmarks Tekniske Bibliotek, Denmark
- Royal Institute of Technology Library, Sweden
- The Japan Information Center of Science and Technology, Japan
- Kinokuniya Book-Store Company, Tokyo
- Iron and Steel Federation of Japan
- International Iron and Steel Institute, Belgium
- Umweltbundesamt (Federal Environmental Agency), Berlin, W.Germany
- Netherlands Consul General, Chicago, IL, U.S.A.
- German Consul General, Chicago, IL, U.S.A.
- Italian Trade Commissioner, Chicago, IL,U.S.A.
- Chamber of Commerce, Luxemburg City, Luxemburg
- Swedish Counsul General, Chicago, IL U.S.A.
- J.G.C. Corporation, Tokyo, Japan
- Nippon Steel Corporation, Tokyo, Japan
- Nippon Kokan Corporation, Kawasaki, Japan
- Krupp Industires and Steel Works, Essen, Germany
- Emission Technical Institute, Baden-Baden, W. Germany
- Water Pollution Research Lab., Stevenage, Herts, England
- British Steel Corporation, Middlesbourgh, Cleveland, United Kingdom
- British Carbonization Research Assn., Wingerworth, Chesterfield, Derbyshire, United Kingdom
- The Metals Society, London, United Kingdom
- Alkalide Inspectorate, United Kingdom
- Hydrotechnics, Inc., New York, NY, U.S.A.
- Engineering Science, Inc., Austin, TX, U.S.A.
- Department of the Environment, Water Directorate, London, United Kingdom
- Aquatechnics, Chicago, IL,U.S.A.
- Gurnham Associates, Chicago, IL, U.S.A.
- Stanley Consultants, Muscatine, IA, U.S.A.
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Sites visited:

- Inland Steel, East Chicago, IN, U.S.A.
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